



## Standoff LIBS: Classification of hazardous residues on painted surfaces



***TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.***

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# Introduction



Standoff LIBS at ARL

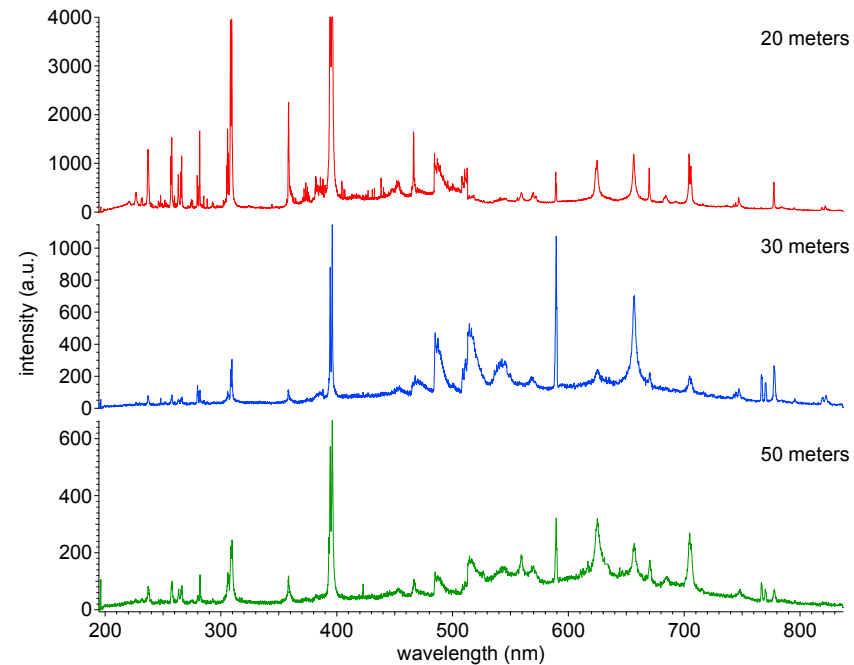
Analysis of painted surfaces

Multivariate analysis of residues on painted surfaces

Conclusions



# Standoff LIBS at ARL



# samples	
explosives	603/695
TPR	87%
non-explosives	4/320
FPR	1.2%



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# Residues on different substrates



RDX, oil, and dust residue

on

Aluminum, rubber, silicone, wood,  
cardboard, travertine

FPR

Aluminum 0%, rubber 0%, silicone  
5%, wood 65%, cardboard 10%,  
travertine 35%

Very different laser-material  
interactions due to diverse  
substrates

Gottfried, J.L., et al., J. Anal. At. Spectrom. 2009, 24, 288-296



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# Goal



Classify explosive residues on substrates with similar compositions

- Minimize differences in laser-material interaction
- Increase number of samples analyzed
- Collect at standoff distance



Use painted surfaces

- Contain organic components; C, H, N, and O
- Different colors will have additional additive components
- Surface roughness, porosity, and hardness more consistent

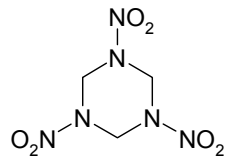


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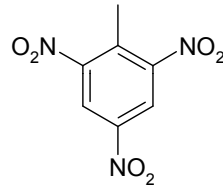
# Samples/substrates



## Explosives



RDX -  $C_3H_6N_6O_6$



TNT -  $C_7H_5N_3O_6$

## Non-explosives

Road dust

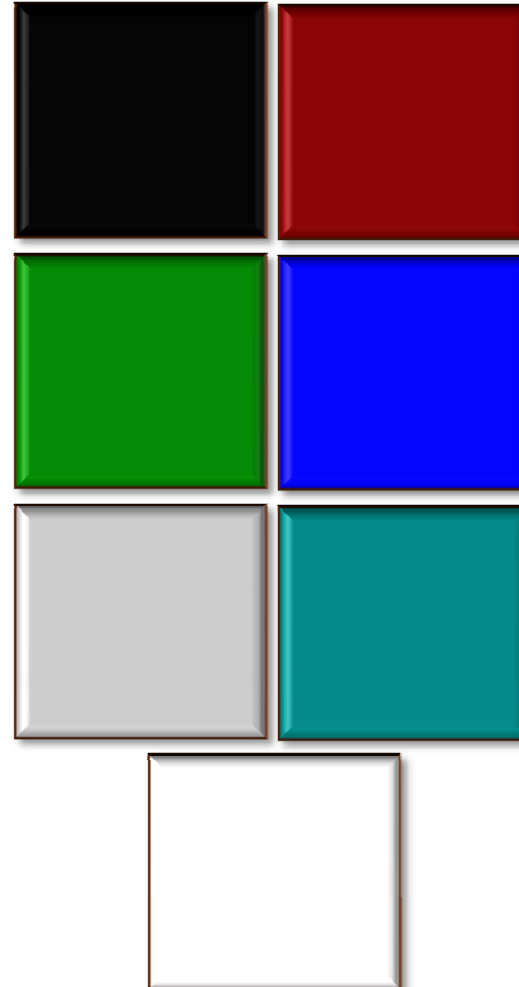
Sand

Oil

Fingerprints

Blank

## Painted Surfaces



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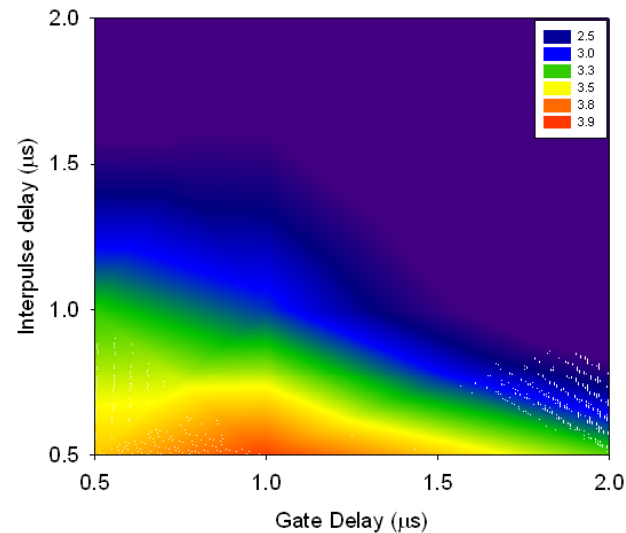
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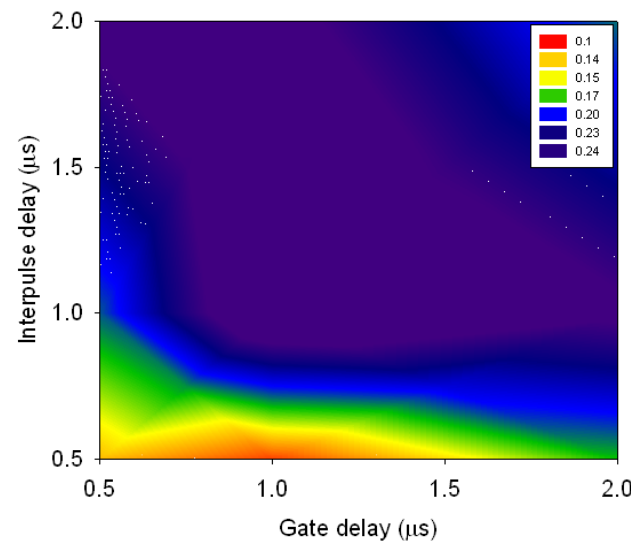
# LIBS experiment



- Laser parameters
  - 1064 nm
  - 335 mJ/ pulse
  - double pulse
- Optimal timing
  - 0.5  $\mu\text{s}$  delay
  - 1  $\mu\text{s}$  interpulse
- 25-30 meters



SNR  
Signal to noise ratio



RMSEC  
Root mean squared  
error of calibration





# Painted surface classification



## Partial least squares discriminant analysis (PLS-DA)

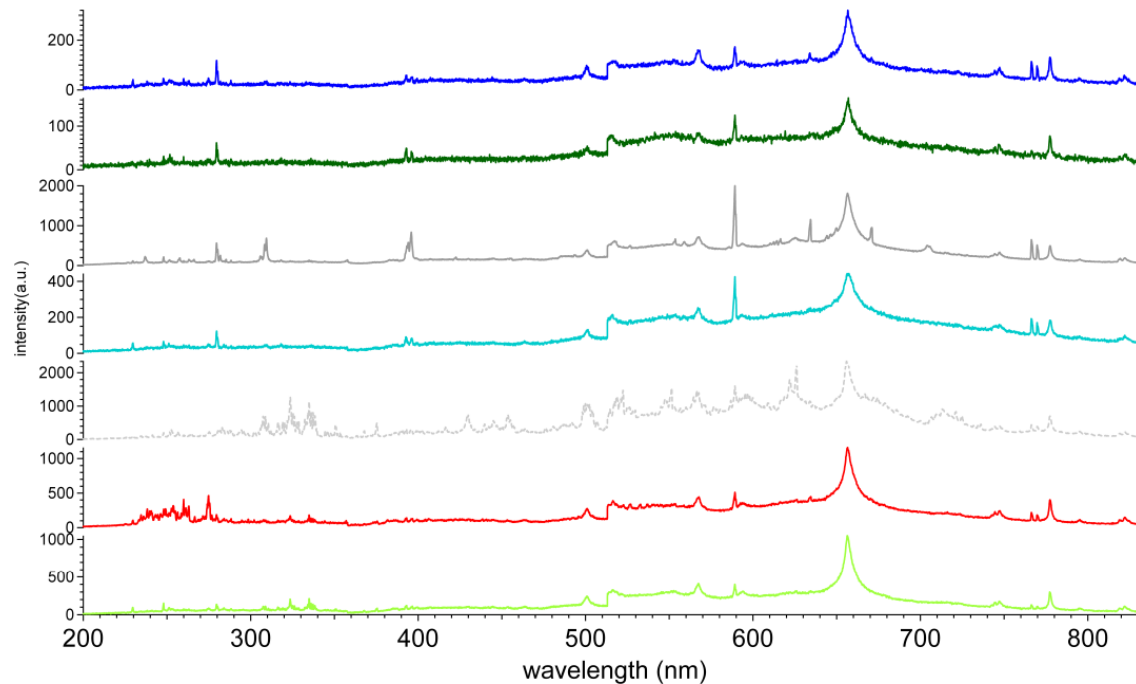
- Supervised, inverse least squares discrimination method
- Generates predictor variables used to classify
- Finds maximum separation between classes

## Collected LIBS spectra

- Model: 495 samples
  - Whole spectra used as variable input
  - 7 classes (based on color)
  - Optimal number of latent variables determined (40)
- Validation: 213 samples



# LIBS spectra of painted surfaces



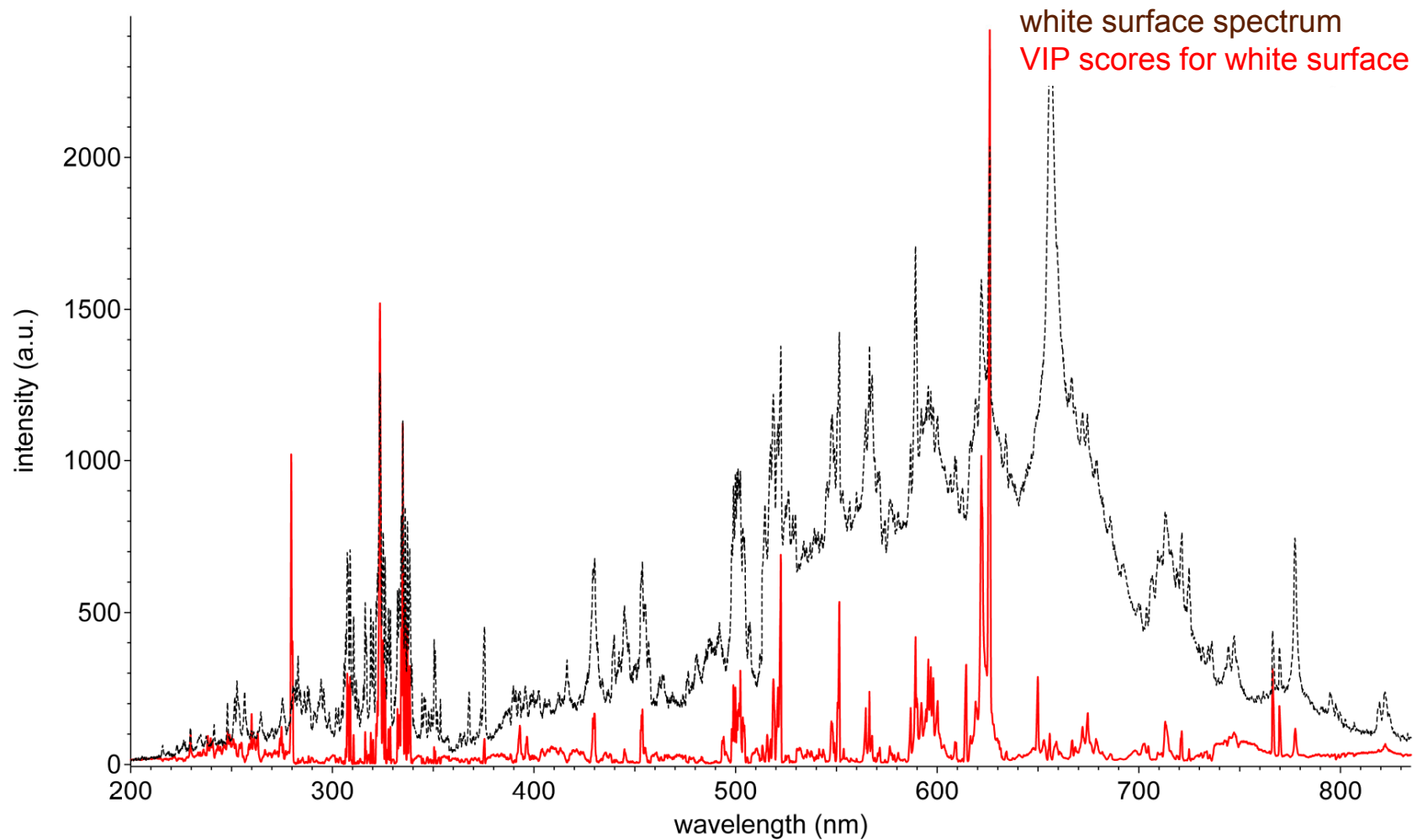
Determine probability of each test sample

- Classified: >75% belongs to correct class
- Misclassified: >75% belongs to incorrect class
- Unclassified: >75% belongs to multiple classes

	Classified	Misclassified	Unclassified
Black	97%	0%	3%
Blue	93%	0%	7%
Dark green	97%	0%	3%
Silver	100%	0%	0%
Teal	100%	0%	0%
Red	100%	0%	0%
White	100%	0%	0%
All	98%	0%	2%



# Variable importance in projection (VIP) scores



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# Residues on painted surface



## PLS-DA model: 414 spectra

- 69 RDX
- 25 TNT
- 70 blank surfaces
- 70 oil
- 60 dust
- 60 fingerprints
- 60 sand

## Three PLS-DA models

- Whole spectra
- Intensity and ratios
- "Fused"

## Model classes based on residue not color

- Explosive
- Blank
- Oil
- Dust
- Fingerprints
- Sand



# Whole spectra model

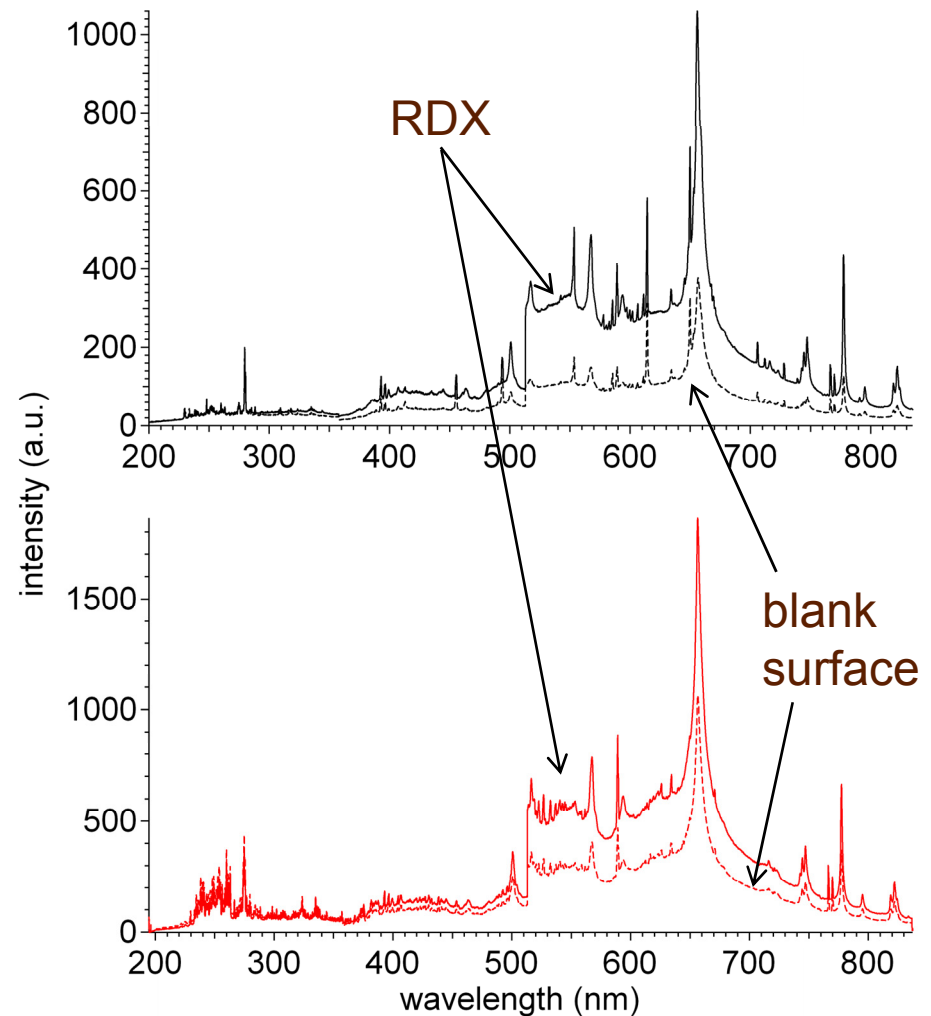


850 test samples

- 210 explosives
- 640 non-explosives

Probability >75% sample belongs to explosive class

TPR 99.5% and FPR 3.1%



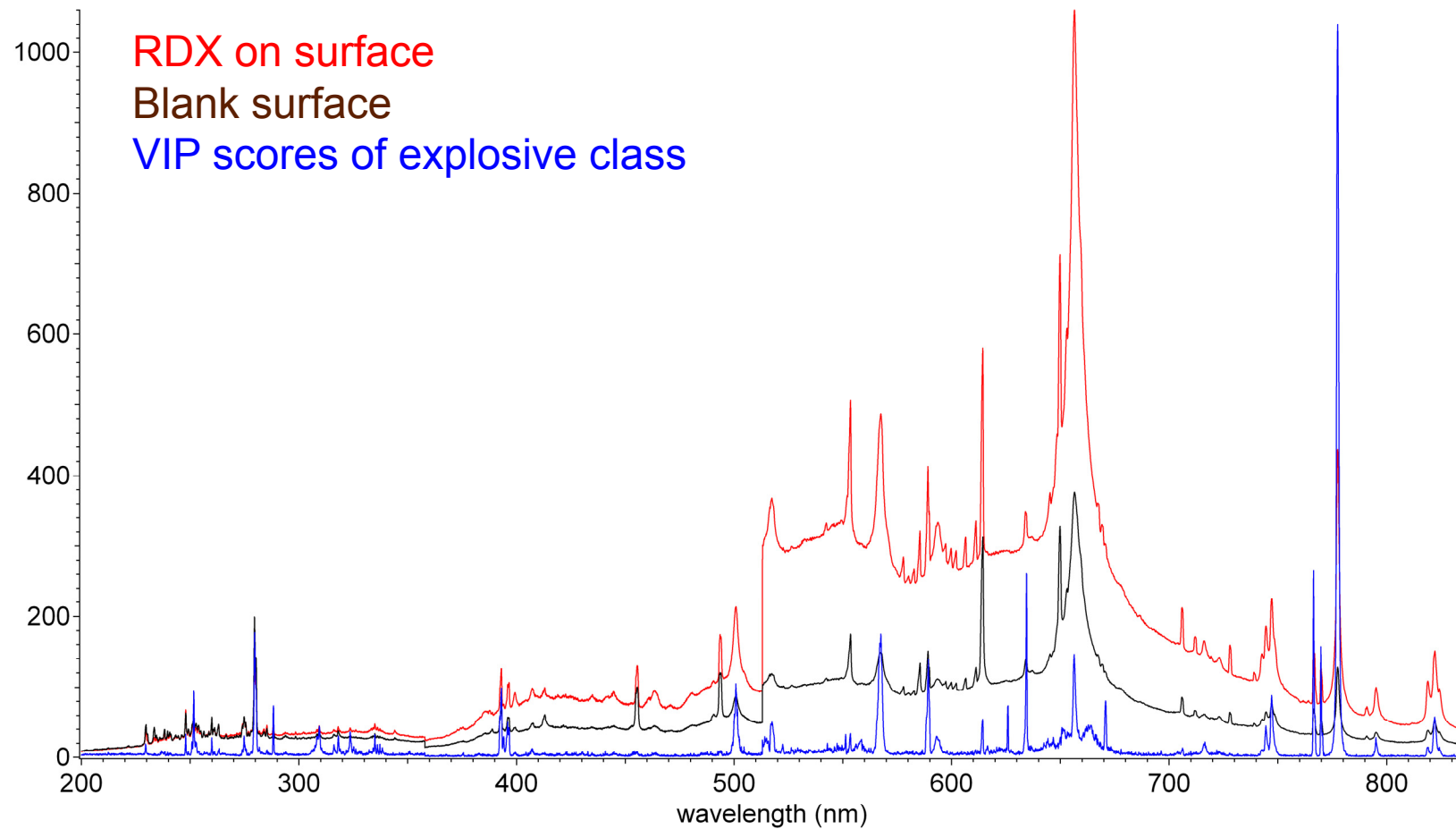
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# VIP scores



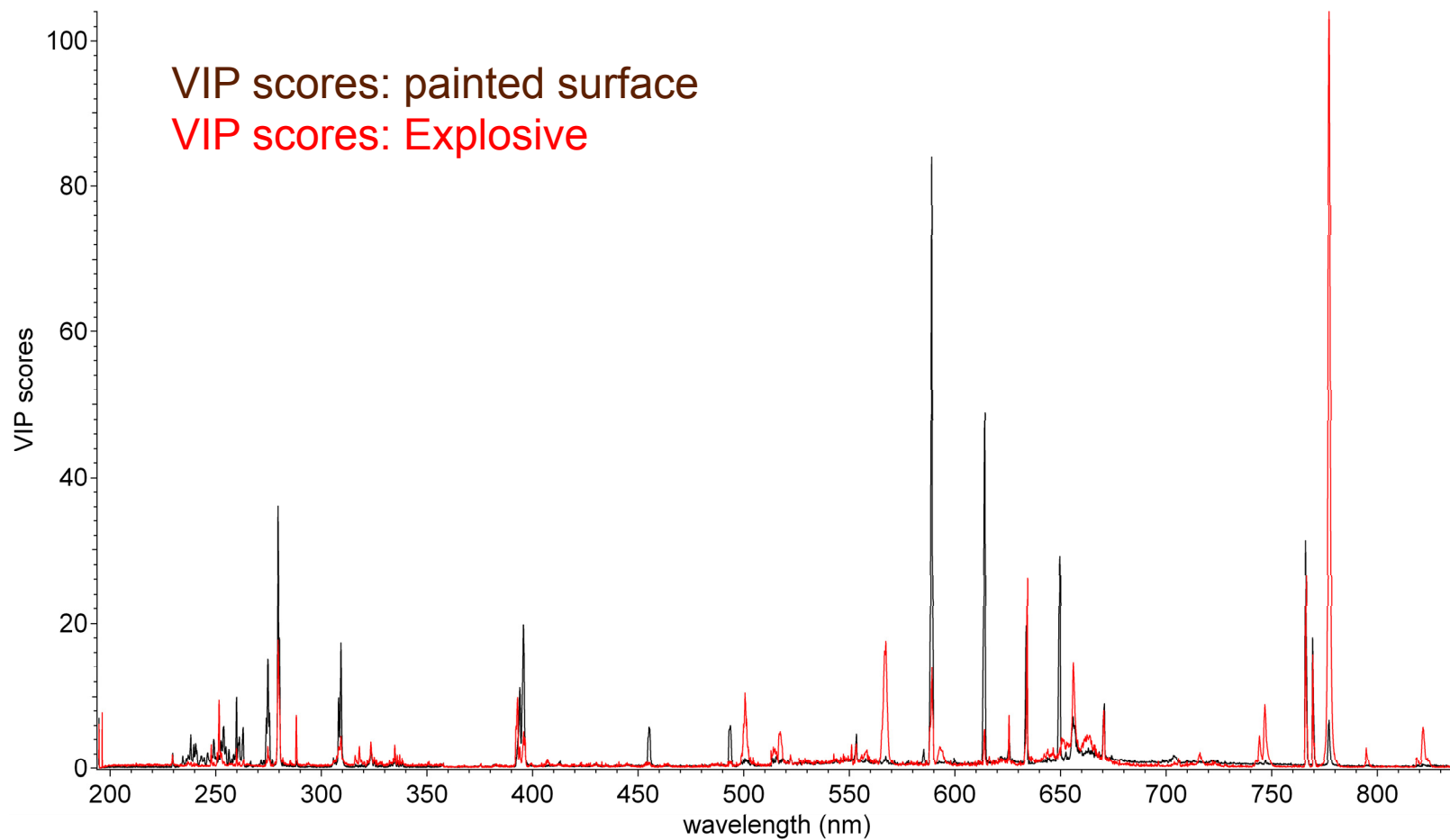
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# VIP scores: explosive class vs. color class



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## Selected intensities and ratios model



3800 test samples

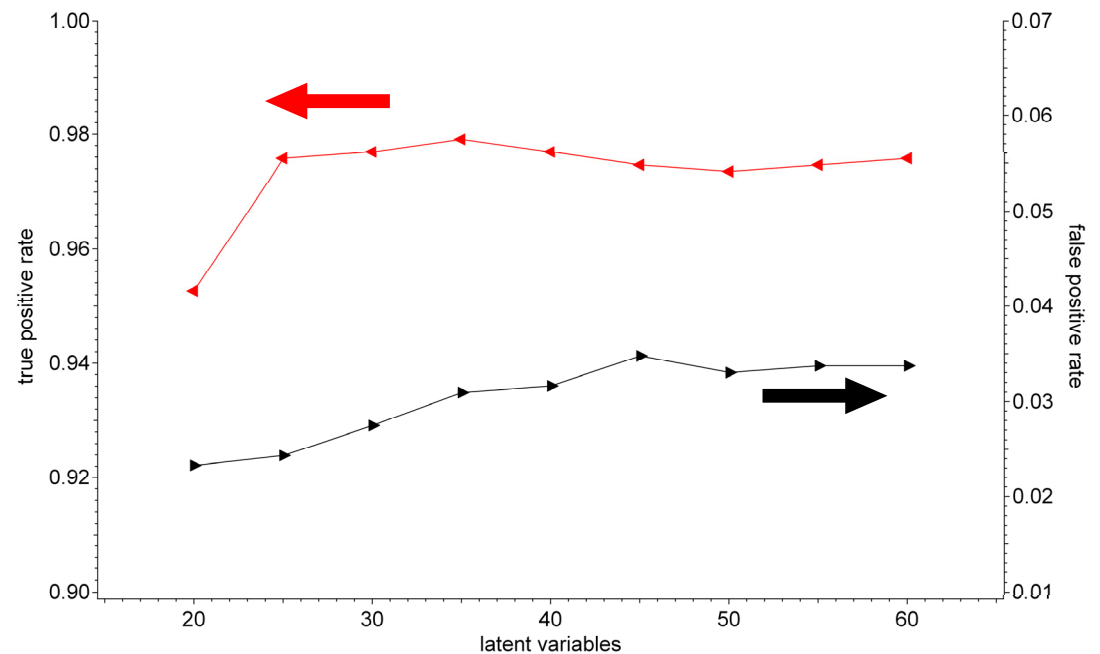
- 908 explosives
- 2876 non-explosives

Used intensities and ratios

- C,H,N and O
- C<sub>2</sub> and CN
- ratios based on non-linear combinations of intensities

TPR 97-98%

FPR 2.5-3.5%





# More testing

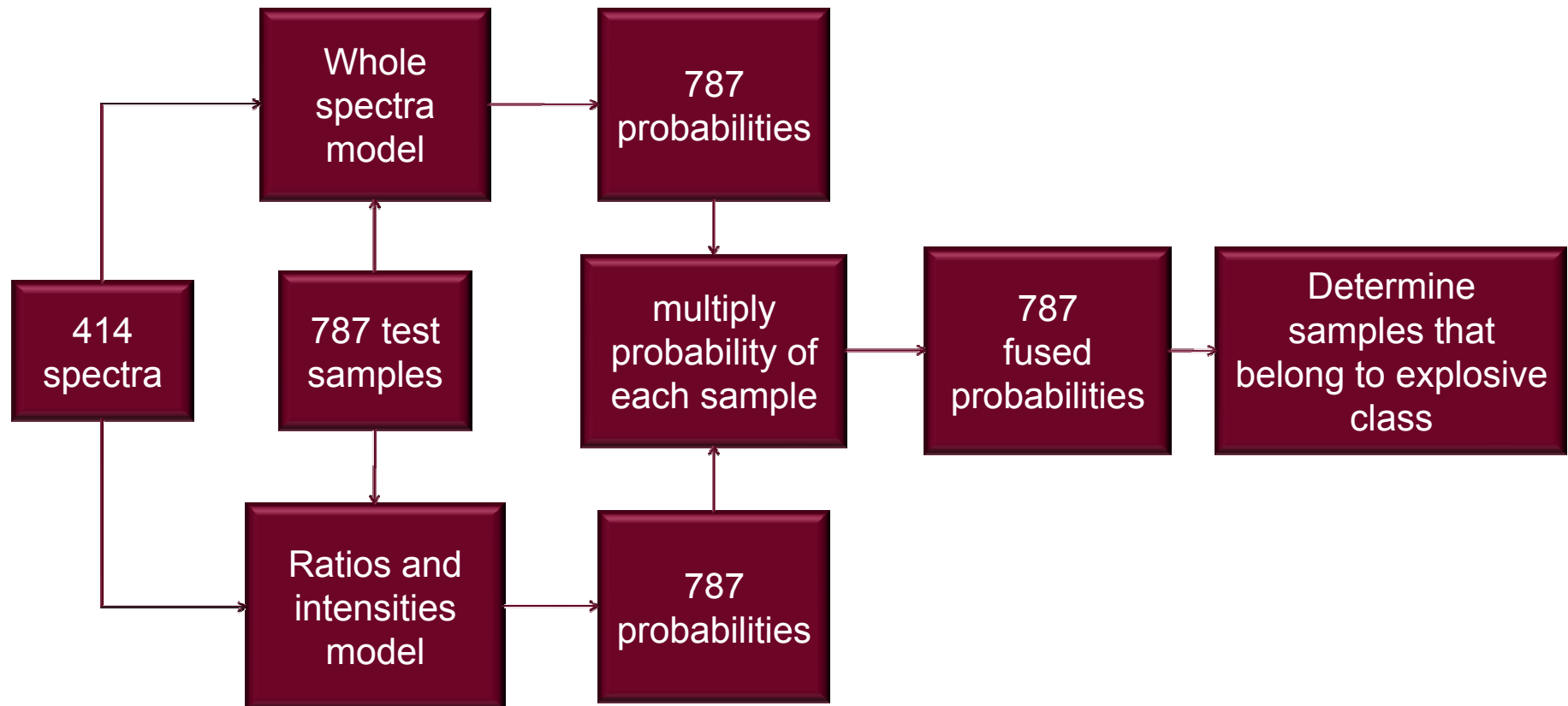


Further tested intensities and ratios model using samples not included in model

- Composition-B (36% TNT, 63% RDX, 1% wax)
- Diesel fuel

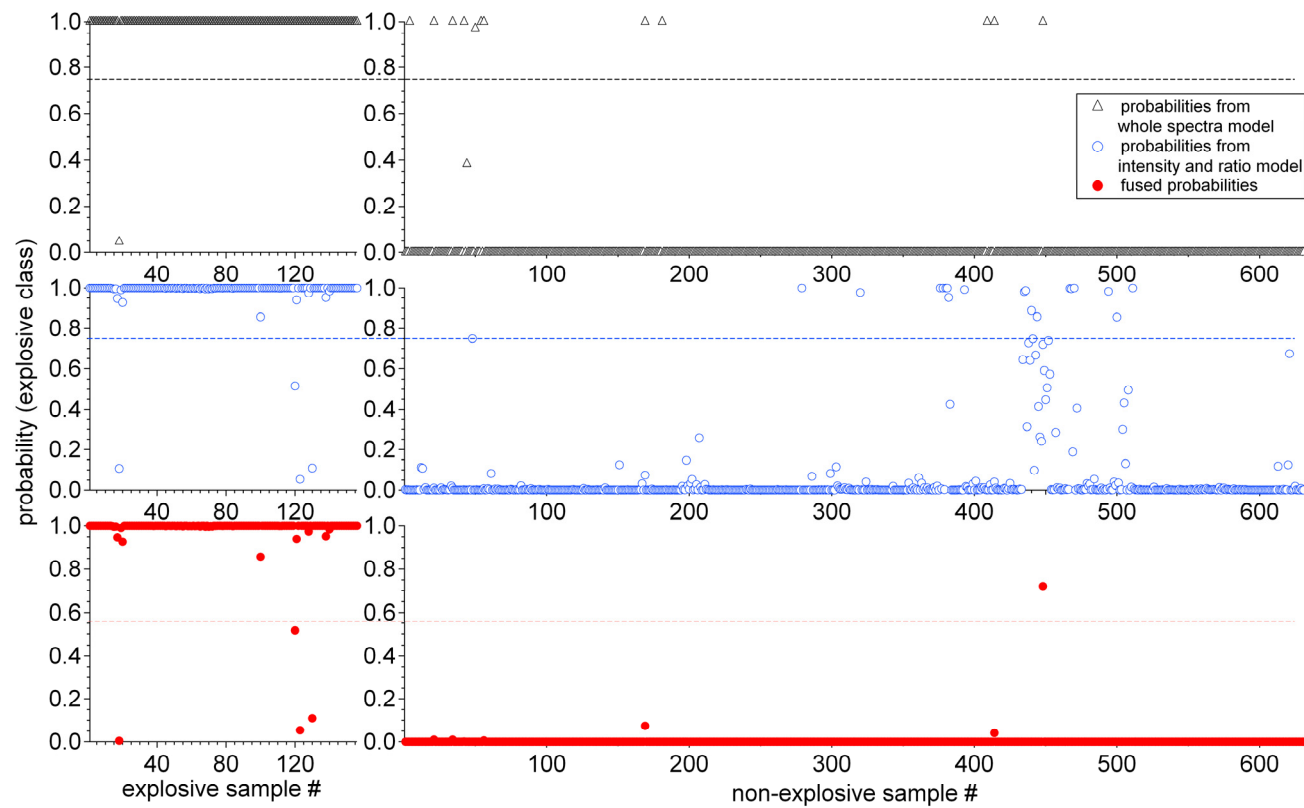
## Results

- 85% TPR (Comp-B) 331 samples
- 4% FPR (diesel) 593 samples





# Probabilities



whole

ratios

fused

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	Whole	Ratio	Fused
TPR	99%	97%	97%
FPR	1.9%	2.9%	0.16%

Classified painted surfaces by color

Classified residues as explosive or non-explosive on painted surfaces

Whole spectra PLS-DA model

- Classification due to constituent elements
- Classification also due to substrate

Ratio PLS-DA model

- Classification can only be due to constituent elements

Fused model decreases false positive rate